CCXXIX.—*Pseudo-ternary Systems containing Sulphur. Part III. The System Sulphur–Sulphur Monochloride.*

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It was noticed by Aronstein and Meihuizen (*Proc. K. Akad. Wetensch. Amsterdam*, 1898, **1**, 1) that a saturated solution of sulphur in sulphur monochloride, S_2Cl_2, after being heated to 170° and chilled, not only failed to deposit sulphur at its saturation temperature but was even capable of dissolving a further amount. This phenomenon was more fully investigated by Aten (*Z. physikal. Chem.*, 1913, **81**, 257). He pointed out that the behaviour of the sulphur solutions could be explained either by the formation of a new modification of sulphur as a result of the rise in temperature, or by the formation of a subchloride as a result of interaction between the dissolved sulphur and the solvent. Both effects could, of course, operate simultaneously. He heated saturated solutions of non-equilibrium sulphur (S_λ) to various temperatures between 50° and 170° and, after chilling them to 25°, 0°, and − 60°, determined the very considerable amounts of S_λ that the solutions would now dissolve before they became once more saturated. As a result of a somewhat elaborate phase-rule analysis of the data obtained, he excluded the possibility of subchloride formation. Further, having found that insoluble or amorphous sulphur is insoluble in cold sulphur monochloride, and assuming that such sulphur is identical with S_μ (the form of sulphur present in equilibrium with S_λ in liquefied sulphur), he concluded that the increase in the amount of sulphur that the solutions would hold after heating could only be explained on the supposition that a new liquid form, S_π, was present. Aten subsequently estimated the amounts of S_π present in liquid equilibrium sulphur at various temperatures (*Z. physikal. Chem.*, 1913, **86**, 10) and found a maximum of 6·7% at 160°. This amount is quite insufficient to account for the large increases in the solvent power of sulphur–sulphur chloride mixtures found when such mixtures are heated and subsequently chilled. For instance, a solution of sulphur in sulphur chloride saturated at 20° contains 17% of S_λ; this solution, after being heated at 100° for a few hours, chilled, and again saturated at 20°, will contain 31% of dissolved S_λ. On Aten's view, this exaltation of the solvent power must be due to the solvent's effect on the internal equilibrium of the dissolved sulphur, considerable amounts of S_π being formed.

The validity of Aten's contention that subchlorides are not formed in sulphur–sulphur monochloride mixtures becomes doubtful in the light of the work of Ruff and Golla (*Z. anorg. Chem.*, 1924, **138**, 33) and of Bruni and Amadori (*Atti R. Accad. Lincei*, 1919, **28**, 217), who obtained indirect evidence for the existence of subchloride molecules. We have therefore sought for direct phase-rule evidence on the question from a detailed study of solid–liquid equilibria in the system, and have determined (i) the solubility curve of sulphur in sulphur monochloride under conditions such that the solutions might be expected to contain only S_λ, and (ii) the temperatures at which the solutions used in (i) were in equilibrium with solid after having been heated to various temperatures until internal equilibrium had been reached and then chilled.

EXPERIMENTAL.

The sulphur used was twice recrystallised from carbon disulphide or toluene and dried at 90°. The sulphur monochloride was distilled in an all-glass apparatus from excess of sulphur, to ensure absence of dichloride, and dried over calcium chloride; it distilled constantly at 138°.

Temperatures of equilibrium between solid phases and solutions were determined by the synthetic method used in previous work on sulphur systems (J., 1926, 1995; 1927, 493). The glass tubes were about 2 cm. in diameter and contained about 3 c.c. of solution. The true solubilities of sulphur in sulphur monochloride (S_λ only in solution) were determined by warming the bulbs in a mechanically stirred paraffin-bath and finding in the usual way the temperatures at which the last small crystal was in equilibrium with the solution. Each bulb was then heated until internal equilibrium had been established at 100°, 148°, 178°, and 230—235° in thermostatic oil-baths. Equilibrium (as indicated by unchanged solid–liquid equilibrium temperatures) was established in 4—5 hours at 100°, 1·5 hours at 148°, and less than an hour at 178° and 230°. After the bulbs had been chilled by plunging them into ice and water (the 230—235° bulbs were chilled for 5 seconds at 100° and then put into ice), crystallisation was induced by cooling, in many cases seeding being necessary as well. A few of the solutions heated to 148°, and many of those heated to 178° and above, deposited monoclinic sulphur on cooling; this could be made to pass into rhombic by warming gently until almost all the crystals had disappeared and then recooling. The data obtained are given below. Solubilities are recorded as g. per 100 g. of solution.

TABLE I.

Solubility of Sulphur in Sulphur Chloride.

Temp.	−9°	2°	4°	10°	21°	28·7°	35·7°	36·8°
S, %	7·34	10·63	11·81	13·52	17·28	22·50	25·79	28·12
Temp.	41°	45·6°	47·6°	54·2°	56°	56·2°	60·2°	61·8°
S, %	30·68	34·91	37·4	42·64	44·7	44·81	49·69	51·70
Temp.	70·2°	71·5°	77·4°	82·4°	83·6°	86·8°	90·5°	92·6°
S, %	60·73	62·18	67·5	73·45	75·4	78·16	82·45	83·4
Temp.	92·5°	97·9°	96·7°	100·8°	101·6°	101·4°	110·3°	
S, %	85·9 (mono)	87·97 (mono)	88·42	89·35 (mono)	90·53 (mono)	93·18	97·02 (mono)	

In Table II solid–liquid equilibrium temperatures are recorded for solutions that had been heated at the specified temperatures and subsequently chilled.

TABLE II.

(*a*) Solid–liquid equilibrium temperatures after preheating at 100°.

Temp.	−30°	−22°	−15·5°	−11°	−6°	−3·3°	2·8°	8·4°
S, %	11·81	14·24	15·75	17·28	20·32	21·91	24·86	26·86
Temp.	14·5°	19°	24°	28·2°	32°	39·4°	46·5°	46·4°
S, %	29·29	30·68	34·91	37·4	40·04	44·7	51·2	51·7
Temp.	56·8°	59·4°	62·2°	65·3°	70·6°	71·5°	74·8°	79·2°
S, %	60·73	62·18	65·0	67·5	70·45	73·45	75·4	78·16
Temp.	85·6°	90·8°	94·4°	94·9°	97·4°			
S, %	82·45	85·9	87·97	88·42	89·35			

(*b*) Solid–liquid equilibrium temperatures after preheating at 148°.

Temp.	−18·5°	−14°	−9·5°	−8°	−4·5°	−0·7°	1°	2·3°
S, %	20·32	22·0	24·86	25·79	26·86	29·29	31·1	32·29
Temp.	5·5°	17°	17·5°	22·8°	27·8°	34°	36·2°	36·5°
S, %	22·15	37·4	37·96	42·64	44·7	50·29	51·2	51·7
Temp.	45° (mono)	53° (rhom)	57°	54·8° (mono)	68·5° (rhom)	70·4°	73·2°	80·5°
S, %	65		67·5	73·45		75·4	78·16	82·45
Temp.	80·8° (mono)	85·4° (rhom)	88·4°	79·6° (mono)	90·6°	109°		
S, %	85·9		87·97	88·42	89·35	97·02		

(*c*) Solid–liquid equilibrium temperatures after preheating at 178°.

Temp.	2·75°	5·0°	10·75°	12·0°	18·5°	23·5°	25·4°	28·0°
S, %	33·15	34·64	37·96	40·96	43·96	46·97	49·78	51·46
Temp.	32·2°	38·0°	41·0°	42·75°	51·5°	62·8°	70·0°	83·8°
S, %	52·8	57·39	61·31	64·76	68·55	73·45	78·16	85·9
Temp.	102·5°							
S, %	93·11							

(*d*) Solid–liquid equilibrium temperatures after preheating at 230—235°.

Temp.	36·6°	44·5°	53·5°	43·0° (mono)	58·6° (rhom)	54·5° (mono)	63·6° (rhom)	73·4°
S, %	55·3	61·31	68·55	70·43		73·06		79·13

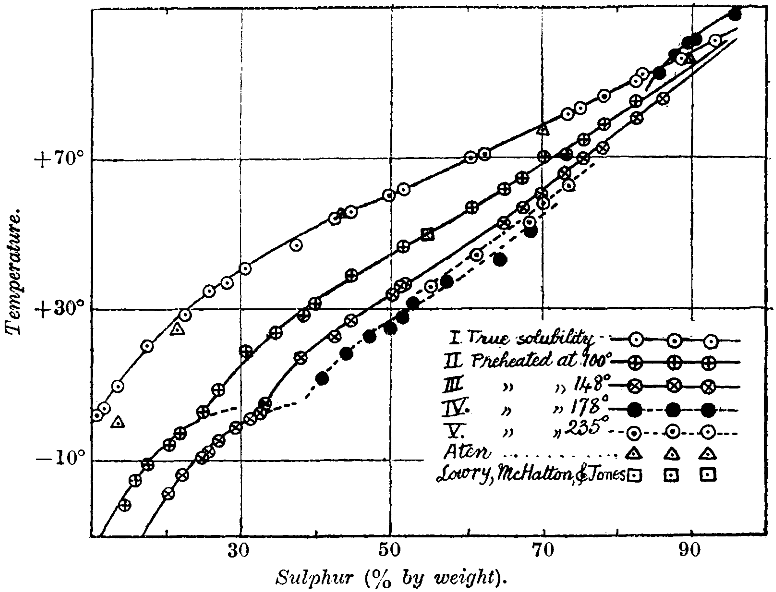
The above results are plotted in the diagram ; some points have been omitted on the sulphur side in order to avoid confusing the curves.

Discussion of Results.

It is necessary that the significance of the curves in the diagram should be made quite clear. Curve I is taken to be the true solubility curve for sulphur in sulphur monochloride, complications due to compound formation or shift of internal equilibrium having been avoided by rapid working. The curve is in good agreement with that of Aten (*loc. cit.*), whose points are indicated on it. Curve II is related to I as follows : At any temperature *t*° a point on Curve I gives the amount of sulphur that must be added to saturate sulphur monochloride without complications. When such a solution is heated at 100° and then chilled, the temperature at which it is now just saturated with sulphur (or other substance capable of giving a crystalline solid phase) is given by a point on Curve II vertically below the first point on Curve I. Curves III, IV, and V are similarly related to Curve I.

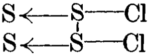
It will be seen that Curves II and III show definite breaks in the neighbourhood of 0°. The lower portions in each case appear to be making for a maximum at a composition of about 34 parts of sulphur added to 66 parts of sulphur monochloride. This composition corresponds to a chloride S_4Cl_2. The solid phases that separate from solutions below 0° do not differ markedly in appearance from rhombic sulphur. That sulphur and sulphur monochloride are not the only substances present in the bulbs was shown, however, by opening them and removing the sulphur monochloride by means of a mercury–vapour pump and an activated-charcoal trap cooled in liquid air. A viscous, yellow oil was obtained, together with crystals of rhombic sulphur. On treatment with water, the oil gave hydrochloric acid with separation of sulphur, thus showing the presence of a chloride of sulphur. This could not be sulphur monochloride, which by itself is entirely volatilised and absorbed under the experimental conditions.

Fig. 1.



Confirmatory evidence that the portions of the Curves II and III correspond to a solid phase other than rhombic or monoclinic sulphur was obtained as follows. A bulb containing 30 parts of sulphur to 70 parts of monochloride was sealed and maintained at 148° for 2 hours. It was then chilled in cold water and placed in liquid air, a transparent glass being obtained. The bulb was opened and the mixture seeded with crystals of rhombic and monoclinic sulphur. No crystallisation occurred on warming and cooling several times. A portion of the liquid contents of the bulb was now placed in a Dewar flask and stirred with a few drops of liquid air. After the latter had evaporated, the glassy mass softened and finally crystallised. A small portion of this crystalline mass was rapidly transferred to the bulb, which had been kept in liquid air. The contents of the bulb now crystallised on warming, a precipitate of small prisms melting at about 0° being obtained. Cooling of the bulb after these crystals had melted did not lead to separation of solid phase unless the liquid was seeded as before; the small crystals of rhombic and monoclinic sulphur originally added to induce crystallisation persisted, however, throughout. The same results were obtained on repetition several times with each of two separate bulbs.

It would thus appear to be established that at least one subchloride of sulphur is formed in heated solutions of sulphur in sulphur monochloride, and it is no longer necessary to suppose with Aten that unusually large amounts of forms of sulphur other than S_λ are formed in such solutions.

It is suggested that the formula of the new subchloride is S_4Cl_2, although there is no information available as to its molecular weight. The simplest formula S_2Cl may be excluded on valency grounds; S_4Cl_2 may reasonably be regarded as  $\begin{array}{l} S \leftarrow S - Cl \\ \quad\;\;\, | \\ S \leftarrow S - Cl \end{array}$, in support of which its low volatility may be noted (compare Sidgwick, "The Electronic Theory of Valency," p. 123).

Lowry, McHatton, and Jones (J., 1927, 746) have examined the whole system sulphur–chlorine. Unfortunately their results for the portion of the system with which we have been concerned are given as a diagram without numerical data. We have calculated one solubility from a point on their graph and find that it lies on our curve for solutions that have been preheated at 100° (see diagram), as would be expected from the fact that their solutions were heated at 96° for a time before equilibrium temperatures were determined (*loc. cit.*, p. 753). Aten's solubilities (*Z. physikal. Chem.*, 1913, **81**, 274) are shown in the diagram, where it will be seen that his points lie satisfactorily on our curve at the higher temperatures. It may be noted that the statement of Lowry, McHatton, and Jones that, after being heated to 170°, sulphur dissolves permanently in sulphur monochloride (*loc. cit.*, p. 753) is incorrect in the light of the data given in Table II (*c* and *d*). Even after preheating at 230—235°, it was possible to determine equilibrium temperatures down to 36·6°. The new chloride, S_4Cl_2, could not, however, be obtained as a solid phase from solutions preheated at 178° or 235°.

The data from the experiments with mixtures preheated at 178° and 235° show that the enhanced solubility effect falls off as the preheating temperature rises, and that it is actually reversed at the highest temperature. The following table gives the solubility of rhombic sulphur at 50° in solutions that have been preheated at T°:

T °	—	100°	148°	178°	235°
S, %	39·5	54·5	62	68	66

In conclusion, it may be mentioned that solutions containing 25—40% of sulphur developed a distinct cloudiness when supercooled to − 75° after preheating at 148°. The opacity disappeared at about − 60° to − 50° on raising the temperature and appeared to be due to the separation of minute liquid droplets. It is thus possible that a metastable two-phase (liquid–liquid) region had been entered. The high viscosity of the solutions prevented adequate agitation of the liquid, so the clearing temperatures could not be accurately observed.

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